

2002/0107133) and Wydra (U.S. Patent No. 3,857,717). These rejections are respectfully traversed.

As discussed during the February 10 interview, it would not have been obvious to combine the coating method of Klotz with Bomberger because those of ordinary skill in the art would not have believed a coating method for magnesium, as disclosed in Klotz, would be applicable on titanium. Specifically, magnesium and titanium have substantially different chemical properties, and corrode in different manners and environments. Furthermore, as will be shown below, it is known in the art that different coating techniques must be used for preventing corrosion in magnesium and titanium. As such, those of ordinary skill in the art would not have believed it would be obvious to try the coating methods of Klotz with the titanium disclosed in Bomberger.

Independent claim 1 recites a method for forming a diffusion barrier on a titanium alloy to prevent corrosion. As discussed during the personal interview, Klotz discloses a method for coating magnesium, or other metals that corrode by water, salt spray or the like, against corrosion. The Office Action asserts that Klotz discloses each step of the method of claim 1. Bomberger discloses that it is possible to coat titanium to prevent corrosion. The Office Action asserts that it would be obvious to use the method of Klotz on titanium, as suggested by Bomberger.

However, this assertion lacks merit for because (1) titanium does not corrode in saltwater, salt spray or the like at standard temperatures and (2) it is known in the art that protective coatings to prevent corrosion must be tailored based on the type of metal, and in particular tailored based on whether the non-ferrous metal to be coated is an active (magnesium) or a noble (titanium) metal.

First, the Office Action asserts that it would be obvious to apply the methods of Klotz to titanium because titanium corrodes in the presence of seawater. However, titanium does

not corrode in the presence of saltwater at room temperature, as magnesium does. Rather, titanium only corrodes at elevated temperatures of 400 C or higher. As such, those of ordinary skill in the art would not have associated titanium as one of the metals that deteriorates in the presence of saltwater mentioned in Klotz.

Second, titanium corrodes via a completely different chemical mechanism than magnesium. Magnesium is an active metal. See Mark's Standard Handbook for Mechanical Engineers, 10th Edition ("Mark's"), page 6-100, and Fig. 6.5.4 (copies attached). As such, magnesium is subject to galvanic corrosion. By contrast, titanium is a noble metal. See Mark's, Fig. 6.5.4. Mark's notes that when forming a protective barrier to prevent corrosion, the barrier properties must be tailored based on whether the metal is noble. See Mark's 6-104. Specifically, 'noble (determined by galvanic series) coatings must be thicker and have a minimum number of pores." See Mark's 6-104. By contrast, "porosity of sacrificial coatings is not critical as long as cathodic protection of the base metal continues." See Mark's, 6-104. Thus, those of ordinary skill in the art know that coatings for metals must be uniquely tailored based on the chemical composition and corrosive properties of the metal to be coated.

The MPEP states that for a combination to be obvious to try, one of ordinary skill must have "a reasonable expectation of success." See MPEP §2143(E). Because those ordinary skill in the art know that titanium and magnesium have such different properties and require unique corrosive resistant coatings, they would not have believed there was such a reasonable expectation of success that a coating method for magnesium, or any other metal that similarly corrodes in seawater, would be operational when applied to titanium. Rather, those of ordinary skill in the art would have believed substantial testing would have been required to adapt the methods of Klotz to titanium, and then tested to ensure success. As such, it would not have been obvious to combine the methods of Klotz to titanium as suggested by the Office Action.

Accordingly, for at least the above reasons, withdrawal of the rejection of claim 1, and claims 2-12 and 23 depending therefrom, is respectfully requested.

In view of the foregoing, it is respectfully submitted that this application is in condition for allowance. Favorable reconsideration and prompt allowance of the claims are earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact the undersigned at the telephone number set forth below.

Respectfully submitted,



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Attachment:

Pages 6-100, 6-104 and 6-105 of Mark's Standard Handbook for Mechanical Engineers, 10th Edition

Date: March 12, 2009

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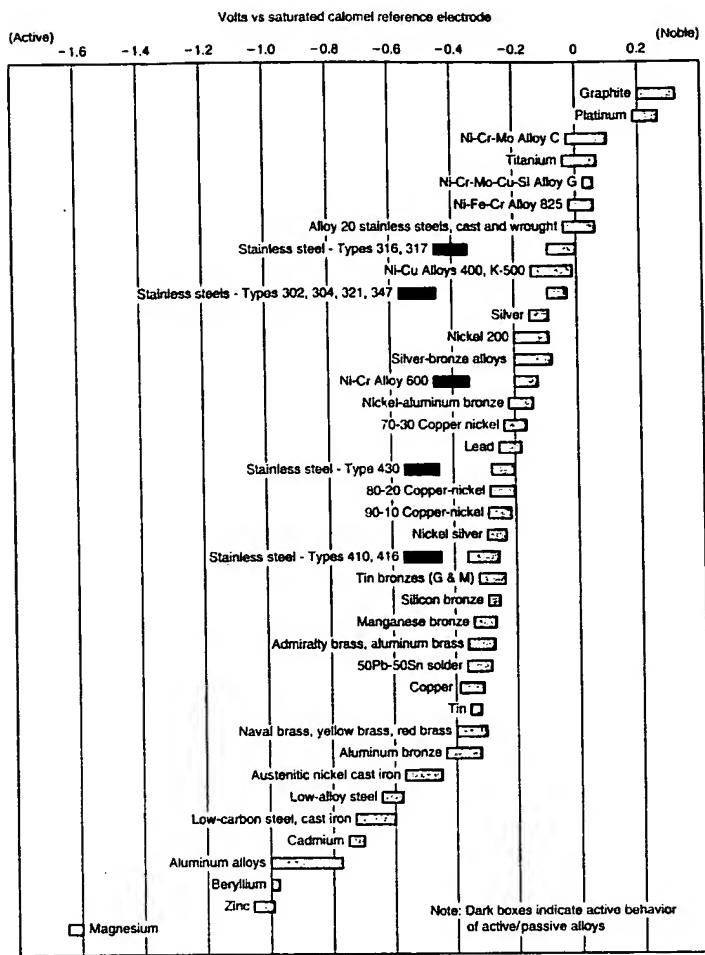


Fig. 6.5.4 Galvanic series for metals and alloys in seawater. Flowing seawater at 2.4 to 4.0 m/s; immersion for 5 to 15 days at 5 to 30°C. (Source: ASTM.)

ions [Eq. (6.5.4)]. Initially, these reactions take place uniformly, both inside and outside the crevice. However, after a short time, oxygen within the crevice is depleted because of restricted convection and oxygen reduction ceases in this area. Because the area within the crevice is much smaller than the external area, oxygen reduction remains virtually unchanged. Once oxygen reduction ceases within the crevice, the continuation of metal dissolution tends to produce an excess of positive charge within the crevice. To maintain charge neutrality, chloride or possibly hydroxide ions migrate into the crevice. This results in an increased concentration of metal chlorides within the crevice, which hydrolyzes in water according to Eq. (6.5.8) to form an insoluble hydroxide and a free acid.



The increased acidity boosts the dissolution rates of most metals and alloys, which increases migration and results in a rapidly accelerating and autocatalytic process. The chloride concentration within crevices exposed to neutral chloride solutions is typically 3 to 10 times higher than that in the bulk solution. The pH within the crevice is 2 to 3. The pH drop with time and critical crevice solution that will cause breakdown in stainless steels can be calculated (Oldfield and Sutton, *Brit. Corrosion J.*, **13**, 1978, p. 13).

Optimum crevice corrosion resistance can be achieved with an active/passive metal that possesses (1) a narrow active-passive transition, (2) a small critical current density, and (3) an extended passive region. Crevice corrosion may be minimized by avoiding riveted, lap, or bolted

joints in favor of properly welded joints, designing vessels for complete drainage and removal of sharp corners and stagnant areas, removing deposits frequently, and using solid, nonabsorbent gaskets (such as Teflon) wherever possible.

Pitting is a form of extremely localized attack forming a cavity or hole in the metal or alloy. Deterioration by pitting is one of the most dangerous types of localized corrosion, but its unanticipated occurrences and propagation rates are difficult to consider in practical engineering designs. Pits are often covered by corrosion products. Depth of pitting is sometimes expressed by the pitting factor, which is the ratio of deepest metal penetration to average metal penetration, as determined by weight loss measurements. A pitting factor of 1 denotes uniform corrosion.

Pitting is usually associated with the breakdown of a passive metal. Breakdown involves the existence of a critical potential E_b , induction time at a potential $>E_b$, presence of aggressive species (Cl^- , H^+ , ClO_4^- , etc.), and discrete sites of attack. Pitting is associated with local imperfections in the passive layer. Nonmetallic inclusions, second-phase precipitates, grain boundaries, scratch lines, dislocations, and other surface inhomogeneities can become initiation sites for pitting (Szklarska-Smialowska, "Pitting of Metals," NACE International, Houston). The induction time before pits initiate may range from days to years. The induction time depends on the metal, the aggressiveness of the environment, and the potential. The induction time tends to decrease if either the potential or the concentration of aggressive species increases.

Once pits are initiated, they continue to grow through an autocatalytic process.

large infrastructural components in real time have been developed for aqueous, soil, and concrete environments using linear polarization resistance (Ansulini et al., *Corrosion/95*, paper 14, NACE International, Houston). Ultrasonic thickness, radiography, or eddy current measurements can evaluate corrosion rates *in situ*. The component surfaces must be clean (free of dirt, paint, and corrosion products) to make measurements. Ultrasonic attenuation techniques have been applied to evaluate the extent of hydrogen damage. A noncontact, nondestructive inspection technique for pitting, SCC, and crevice corrosion has been developed using digital speckle correlation (Jin and Chiang, *Corrosion/95*, paper 535, NACE International, Houston). An ASTM publication [Baboian (ed.), "Manual 20—Corrosion Tests and Standards: Application and Interpretation," ASTM, Philadelphia] provides a detailed, comprehensive reference for field and laboratory testing in different environments for metals and alloys, coatings, and composites. It includes testing for different corrosion forms and for different industrial applications.

CORROSION PREVENTION OR REDUCTION METHODS

The basis of corrosion prevention or reduction methods involves restricting or controlling anodic and/or cathodic portions of corrosion reactions, changing the environmental variables, or breaking the electrical contact between anodes and cathodes. Corrosion prevention or reduction methods include (1) proper materials selection, (2) design, (3) coatings, (4) use of inhibitors, (5) anodic protection, and (6) cathodic protection [Treseder et al. (eds.), "NACE Corrosion Engineer's Reference Book," 2d ed., NACE International, Houston].

The most common method to reduce corrosion is *selecting the right material* for the environmental conditions and applications. Ferrous and nonferrous metals and alloys, thermoplastics, nonmetallic linings, resin coatings, composites, glass, concrete, and nonmetal elements are a few of the materials available for selection. Experience and data, either in-house or from outside vendors and fabricators, may assist in the materials selection process. Many materials can be eliminated by service conditions (temperature, pressure, strength, chemical compatibility). Corrosion data for a particular chemical or environment may be obtained through a literature survey ("Corrosion Abstracts," NACE International; "Corrosion Data Survey—Metals Section," 6th ed., "Corrosion Data Survey—Nonmetals Section," NACE International, Houston) or from expert systems or databases. Different organizations (ASTM, ASM International, ASME, NACE International) may offer references to help solve problems and make predictions about the corrosion behavior of candidate materials. The material should be cost-effective and resistant to the various forms of corrosion (discussed earlier) that may be encountered in its application. General rules may be applied to determine the resistance of metals and alloys. For reducing or nonoxidizing environments (such as air-free acids and aqueous solutions), nickel, copper, and their alloys are usually satisfactory. For oxidizing conditions, chromium alloys are used, while in extremely powerful oxidizing environments, titanium and its alloys have shown superior resistance. The corrosion resistance of chromium and titanium can be enhanced in hot, concentrated oxidizer-free acid by small additions of platinum, palladium, or rhodium.

Many costs related to corrosion could be eliminated by *proper design*. The designer should have a credible knowledge of corrosion or should work in cooperation with a materials and corrosion engineer. The design should avoid gaps or structures where dirt or deposits could easily form crevices; horizontal faces should slope for easy drainage. Tanks should be properly supported and should employ the use of drip skirts and dished, fatigue-resistant bottoms ("Guidelines for the Welded Fabrication of Nickel Alloys for Corrosion-Resistant Service," part 3, Nickel Development Institute, Toronto, Canada). Connections should not be made of dissimilar metals or alloys widely separated in the galvanic series for lap joints or fasteners, if possible. Welded joints should avoid crevices, microstructural segregation, and high residual or applied stresses. Positioning of parts should take into account prevailing environmental conditions. The design should avoid local differences in concentration, temperature, and velocity or turbulence. All parts requiring maintenance or replacement must be easily accessible. All parts to be coated must be accessible for the coating application.

Protective coatings are used to provide an effective barrier to corrosion and include metallic, chemical conversion, inorganic nonmetallic, and organic coatings. Before the application of an effective coating on metals and alloys, it is necessary to clean the surface carefully to remove, dirt, grease, salts, and oxides such as mill scale and rust. Metallic coatings may be applied by cladding, electrodeposition (copper, aluminum, nickel, tin, chromium, silver, zinc, gold), hot dipping (tin, zinc, galvanizing, lead, and aluminum), diffusion (chromium-chromium, zinc-silver-zinc, boron, silicon, aluminum-calorizing or aluminum-tin, titanium, molybdenum), metallizing or flame spraying (zinc, aluminum, lead, tin, stainless steels), vacuum evaporation (aluminum), implantation, and other methods. All commercially prepared coatings are porous to some degree. Corrosion or galvanic action may influence the performance of the metal coating. Noble (determined by the galvanic series) coatings must be thicker and have a minimum number of pores and small pore size to delay entry of any deleterious fluid. Some pores of noble metal coatings are filled with an organic lacquer or a second lower-melting-point metal is diffused into the initial coating. Sacrificial or cathodic coatings such as cadmium, zinc, and in some environments, tin and aluminum, cathodically protect the base metal. Porosity of sacrificial coatings is not critical as long as cathodic protection of the base metal continues. Higher solution conductivity allows larger defects in the sacrificial coating; thicker coatings provide longer times of effective cathodic protection.

Conversion coatings are produced by electrochemical reaction of a metal surface to form adherent, protective corrosion products. Anodizing aluminum forms a protective film of Al_2O_3 . Phosphate and chromate treatments provide temporary corrosion resistance and usually a basis for painting. Inorganic nonmetallic coatings include vitreous enamels, glass linings, cement, or porcelain enamels bonded on metals. Susceptibility to mechanical damage and cracking by thermal shock are major disadvantages of these coatings. An inorganic coating must be perfect and defect-free unless cathodic protection is applied.

Paints, lacquers, coal-tar or asphalt enamels, waxes, and varnishes are typical organic coatings. Converted epoxy, epoxy polyester, moisture-cured polyurethane, vinyl, chlorinated rubber, epoxy ester, oil-modified phenolics, and zinc-rich organic coatings are other barriers used to control corrosion. Paints, which are a mixture of insoluble particles of pigments (for example, TiO_2 , Pb_3O_4 , Fe_2O_3 , and ZnCrO_4) in a continuous organic or aqueous vehicle such as linseed or tung oil, are the most common organic coatings. All paints are permeable to water and oxygen to some degree and are subject to mechanical damage and eventual breakdown. Inhibitor and antifouling agents are added to improve protection against corrosion. Underground pipelines and tanks should be covered with thicker coatings of asphalt or bituminous paints, in conjunction with cloth or plastic wrapping. Polyester and polyethylene have been used for tank linings and as coatings for tank bottoms (Munger, "Corrosion Prevention by Protective Coatings," NACE International, Houston).

Inhibitors, when added above a threshold concentration, decrease the corrosion rate of a material in an environment. If the level of an inhibitor is below the threshold concentration, corrosion could occur more quickly than if the inhibitor were completely absent. Inhibitors may be organic or inorganic and fall into several different classes: (1) passivators or oxidizers, (2) precipitators, (3) cathodic or anodic, (4) organic adsorbents, (5) vapor phase, and (6) slushing compounds. Any one inhibitor may be found in one or more classifications. Factors such as temperature, fluid velocity, pH, salinity, cost, solubility, interfering species, and metal or alloy may determine both the effectiveness and the choice of inhibitor. Federal EPA regulations may limit inhibitor choice (such as chromate use) based on its toxicity and disposal requirement.

Passivators in contact with the metal surface act as depolarizers, initiating high anodic current densities and shifting the potential into the passivation range of active/passive metal and alloys. However, the

in concentrations below 10^{-3} to 10^{-4} M, these inhibitors can be passivating. Passivating inhibitors are anodic inhibitors and may include anions such as chromate, nitrite, and nitrate. Phosphate, borate, and tungstate require oxygen to passivate steel and are considered nonoxidizing. Nonoxidizing sodium benzoate, cinnamate, and polyphosphate compounds effectively passivate iron in the near-neutral pH by facilitating oxygen adsorption. Alkaline compounds (NaOH, Na₂CO₃, Na₃B₅O₇, and Na₂O-nSiO₄) indirectly assist iron passivation by increasing oxygen adsorption.

Protectants are film-forming compounds which create a general coating over the metal surface and subsequently indirectly interfere with both anodes and cathodes. Silicates and phosphates in conjunction with calcium provide effective inhibition by forming deposits. Calcium and magnesium interfere with inhibition by silicates; 2 to 3 ppm of polyphosphate is added to overcome this. The levels of calcium and phosphate must be balanced for effective calcium phosphate inhibition. Addition of a zinc salt often improves polyphosphate inhibition.

Cathodic inhibitors (cathodic poisons, cathodic precipitates, oxygen scavengers) are generally cations which migrate toward cathode surfaces where they are selectively precipitated either chemically or electrokinetically to increase circuit resistance and restrict diffusion of reactive species to the cathodes. Cathodic poisons interfere with and reduce the HER, thereby slowing the corrosion process. Depending on the inhibitor, arsenic, bismuth, antimony, sulfides, and selenides are useful cathodic poisons. Sulfides and arsenic can cause hydrogen blistering and hydrogen embrittlement. Cathodic precipitation-type inhibitors include calcium and magnesium carbonates and zinc sulfate in natural waters. The pH must be adjusted to be effective. Oxygen scavengers inhibit corrosion, either alone or with another inhibitor, to prevent cathodic depolarization. Sodium sulfite, hydrazine, carbohydrazide, hydrazine, methylthioketoxime, and diethylhydroxylamine are oxygen scavengers.

Organic inhibitors, in general, affect the entire surface of a corroding metal and affect both the cathode and anode to differing degrees, depending on the potential and the structure or size of the molecule. Cathodic positively charged inhibitors such as amines and anionic, negatively charged inhibitors such as sulfonates will be adsorbed differentially depending on whether the metal surface is negatively or positively charged. Soluble organic inhibitors form a protective layer only a few molecules thick; if an insoluble organic inhibitor is added, the film may become about 0.003 in (76 μ m) thick. Thick films show limited persistence by continuing to inhibit even when the inhibitor is no longer being injected into the system.

Vapor phase inhibitors consist of volatile aliphatic and cyclic amines and nitriles that possess high vapor pressures. Such inhibitors are placed in the vicinity of the metal to be protected (e.g., inhibitor-impregnated sludge), which transfers the inhibiting species to the metal by sublimation or condensation where they adsorb on the surface and retard the anodic, cathodic, or both corrosion processes. This inhibitor protects against water and/or oxygen. Vapor-phase inhibitors are usually effective only if used in closed spaces and are used primarily to retard atmospheric corrosion. Slushing compounds are polar inorganic or organic additives in oil, grease, or wax that adsorb on the metal surface to form a continuous protective film. Suitable additives include organic amines, alkali and alkaline-earth metal salts of sulfonated oils, sodium nitrite, and organic chromates [Nathan (ed.), "Corrosion Inhibitors," NACE International, Houston].

Anodic protection is based on the formation of a protective film on the metal by externally applied anodic currents. Figure 6.5.5 illustrates the potential range in which anodic protection is achieved. The applied anodic current density is equal to the difference between the total oxidation and reduction rates of the system, or $i_{app} = i_{red} - i_{ox}$. The potential range in which anodic protection is achieved is the protection range or passive region. At the optimum potential E_A , the applied current is approximately 1 μ A/cm². Anodic protection is limited to active/passive metals and alloys and can be utilized in environments ranging from weak to very aggressive. The applied current is usually related to the corrosion of the protected system which can be used to control the instantaneous corrosion rate. Operating conditions in the

field usually can be accurately and quickly determined by electrochemical laboratory tests (Riggs and Locke, "Anodic Protection—Theory and Practice in the Prevention of Corrosion," Plenum Press, New York).

Cathodic protection (CP) controls corrosion by supplying electrons to a metal structure, thereby suppressing metal dissolution and increasing hydrogen evolution. Figure 6.5.5 shows that when an applied cathodic current density ($i_{app} = i_{red} - i_{ox}$) of 10,000 μ A/cm² on a bare metal surface shifts the potential in the negative or active direction to E_c , the corrosion rate has been reduced to 1 μ A/cm². CP is applicable to all

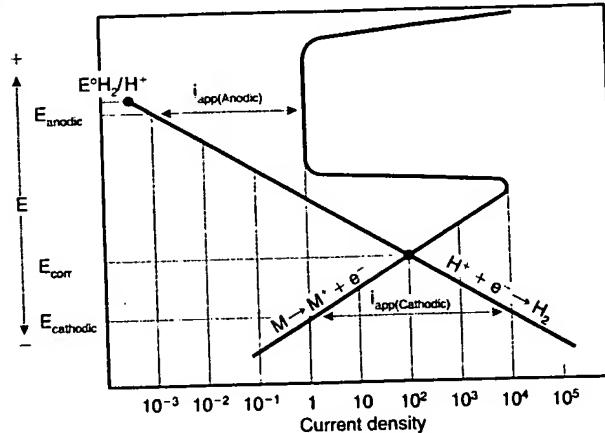


Fig. 6.5.5 Effect of applied anodic and cathodic currents on behavior of an active/passive alloy necessary for anodic and cathodic protection, respectively. (Adapted from "Fontana's Book on Corrosive Engineering," McGraw-Hill.)

metals and alloys and is common for use in aqueous and soil environments. CP can be accomplished by (1) impressed current from an external power source through an inert anode or (2) the use of galvanic couplings by sacrificial anodes. Sacrificial anodes include zinc, aluminum, magnesium, and alloys containing these metals. The total protective current is directly proportional to the surface area of the metal being protected; hence, CP is combined with surface coatings where only the coating pores or holidays and damaged spots need be cathodically protected [e.g., for 10 miles of bare pipe, a current of 500 A would be required, while for 10 miles of a superior coated pipe ($5 \times 10^6 \Omega/\text{ft}^2$) 0.03 A would be required]. The polarization potential can be measured versus a reference, commonly saturated Cu/CuSO₄. The criterion for proper CP is -0.85 V versus this reference electrode. Overprotection by CP (denoted by potentials less than -0.85 V) can lead to blistering and debonding of pipe coatings and hydrogen embrittlement of steel from hydrogen gas evolution. Another problem with CP involves stray currents to unintended structures. The proper CP for a system is determined empirically and must resolve a number of factors to be effective (Peabody, "Control of Pipeline Corrosion," NACE International, Houston; Morgan, "Cathodic Protection," 2d ed., NACE International, Houston).

CORROSION IN INDUSTRIAL AND UTILITY STEAM-GENERATING SYSTEMS

Boiler Corrosion

Corrosion can be initiated from the fireside or the waterside of the surfaces in the boiler. In addition to corrosion, there are a number of other types of failure mechanisms for boiler components, including fatigue, erosion, overheating, manufacturing defects, and maintenance problems. Some of the actual failure mechanisms are combinations of mechanical and chemical mechanisms, such as corrosion fatigue and stress corrosion cracking (SCC). The identification, cause(s), and corrective action(s) for each type of failure mechanism are presented in